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An update to the ambient ratio method for 1-h NO_2 air quality standards dispersion modeling

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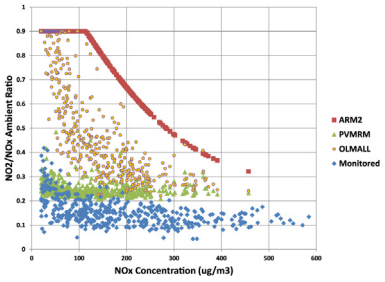
HIGHLIGHTS

- Ambient NO_X monitoring data was used to determine the conversion of NO to NO_2 gases.
- A conversion equation was developed and incorporated into EPA's AERMOD model.
- Performance testing of this method was conducted.
- The results indicate that the method conservatively estimates ambient NO_2 levels.
- EPA has approved ARM2 subject to certain limitations as discussed in this paper.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrogen oxide (NO_X) gases are typically emitted by fuel combustion sources in the form of nitric oxide (NO), which then reacts with ozone and other oxidants in the atmosphere to convert a portion of the NO to nitrogen dioxide (NO_2). EPA has promulgated a 1-h average National Ambient Air Quality Standard (NAAQS) for NO_2, and major sources of NO_X emissions must estimate their NO_2 air quality impacts as part of EPA's air quality permitting programs. The AERMOD dispersion model has been developed by EPA for these air quality impact analyses, and AERMOD contains three different NO to NO_2 conversion methods for estimating the ambient concentrations of NO_2. This paper describes a refinement to one of the methods, the Ambient Ratio Method version 2 (ARM2). ARM2 is an empirical approach that uses a variable conversion factor, based on an analysis of ambient air measurements of NO and NO_2, to estimate the portion of the AERMOD predicted air concentration of total NO_X species that is in the form of NO_2. The performance of ARM2 has been evaluated and found to compare well to actual ambient measurements and to other more complex EPA conversion methods. EPA has included ARM2 as a "beta-testing" option in AERMOD version 14134, and provided guidance on the use of ARM2 for regulatory modeling analyses in a September 2014 memorandum. This paper also discusses this recent EPA guidance.

1. Introduction

EPA has established a National Ambient Air Quality Standard (NAAQS) for nitrogen dioxide (NO_2) at a level of 100 ppbv (188.7 μg/m^3) averaged over a 1-h period. When EPA or a state regulatory air agency issues a New Source Review (NSR) construction permit for major sources of air pollution, one of the permitting requirements is an air quality impact analysis that demonstrates compliance with the NAAQS. The air impact analysis is performed using EPA-

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approved air quality dispersion models such as the AERMOD model. AERMOD is a steady-state Gaussian plume model that contains algorithms to simulate plume rise and turbulent atmospheric mixing and dispersion processes.

NO_X gases are usually emitted by fuel combustion sources in the form of nitric oxide (NO), and in smaller quantities as NO_2 gas (Integrated Science Assess, July 2008). NO gases in the emission plume mixes with the atmosphere and reacts with ozone and other oxidants to oxidize a portion of the NO to NO_2. There are numerous other atmospheric reactions of NO_X species; these include further oxidation of NO_2 to nitrate radical (NO_3) and nitric acid (HNO_3), as well as photo-dissociation of NO_2 back to NO through the absorption of UV radiation during the daytime (Rethinking the Ozone Prob, 1991). However, during the early stages of the dispersion of a NO_X emission plume (i.e., at distances ranging from approximately 0.1 to 10 km over time intervals of 10–300 min), the principal NO_X reaction is NO oxidation by ozone to form NO_2 (Karamchandani et al., 1998). Janssen (Janssen et al., 1990) analyzed NO_X measurements in power plant plumes and observed that the oxidation of NO to NO_2 in plumes was limited by the interaction between the chemical kinetics of the oxidation process and the mixing of the plume with the ambient atmosphere.

During the initial NSR implementation of the 1-h NO_2 NAAQS in 2010, EPA acknowledged that AERMOD and the existing modeling guidance did not address how to use AERMOD to estimate the conversion of NO emissions to 1-h averaged NO_2 ambient concentrations. Therefore, EPA issued two memorandums in 2010 (Fox, 2010) and 2011 (Fox, 2011) that provided guidance on how to use AERMOD to perform 1-h NO_2 NAAQS analyses. EPA also issued additional guidance on September 30, 2014, that addressed the use of ARM2 and highlighted the importance of the in-stack ratios (ISR) of NO_2/NO_X emissions for NAAQS modeling analyses (Brode, 2014).

EPA's "Guideline on Air Quality Models" (Code of Federal Regulatio) describes the three EPA recommended conversion methods. The three methods are arranged in order or "tiers" from the most simple and conservative to the most refined:

- Tier 1, in which it is assumed that all modeled emissions of total NO_X (NO plus NO_2 emissions) have been fully converted to NO_2. This is a very conservative method for estimating ambient NO_2 concentrations.
- Tier 2 is the Ambient Ratio Method (ARM), which applies an empirically derived conversion factor to the modeled NO_X concentration. This factor is based on observed NO_2/NO_X ratios of monitoring data, and EPA has recommended a fixed conversion factor of 0.8 for modeling 1-h NO_2 concentrations.
- The Tier 3 methods are the Ozone Limiting Method (OLM) and the Plume Volume Molar Ratio Method (PVMRM). Both of these methods assume that ozone in the atmosphere instantaneously reacts with the emitted NO in the plume to form NO_2. The OLM method assumes that atmospheric ozone is instantly mixed throughout the plume, while the PVMRM method considers the number of moles of atmospheric ozone that could be entrained into the NO emission plume based on the extent of the plume dispersion. Although these methods are more refined than the empirical ARM, the assumptions used do not account for the mixing rates of the plumes with the surrounding atmosphere and the chemical reaction rates, which do affect the resultant NO_2 concentrations in the atmosphere. These Tier 3 methods require the identification of representative ozone monitoring data for the study area, and data on the actual in-stack ratios of the emitted NO and NO2 gaseous species.

The ARM method was originally developed by Chu and Meyer (1991). They analyzed historical ambient NO and NO_2 monitoring data to establish a conservative conversion factor for estimating the portion of the model predicted total NO_X concentration that is in the form of NO_2 for annual averaging intervals They reviewed ambient monitoring data from a large number of sites throughout the US for the period 1987–1989, and for each site calculated the annual average ambient NO_2 and NO_X concentrations and the ambient NO_2/NO_X ratio (i.e., the observed conversion factor). The 90th percentile of the observed conversion factors was selected as a conservative, upper bound estimate that established the current EPA recommended Tier 2 conversion factor of 0.8 for annual average NO_2 AERMOD modeling.

ARM uses a conservative, fixed conversion factor. However, Chu and Meyer's data indicates that the NO_2/NO_X conversion factor is variable and increases with distance/time from the emission source (as there is more time for oxidation to NO_2, and concurrently the total NO_X concentration decreases because of increased dilution of the plume). Other field studies also have shown these same trends between observed conversion factors and total NO_X concentrations. Wang presents results from four short-term monitoring tests near roadways (Wang et al., 2011). In this study the observed NO_2/NO_X ratios varied from approximately 0.3 to 0.8. Janssen studied NO_X chemistry in power-plant plumes and reports the same variability of NO_2/NO_X ratio as a function of distance and as a function of the total measured NO_X concentration (Janssen et al., 1991). The implication of these observations is that the application of a conservative, fixed ARM conversion factor will likely overestimate the actual conversion and resulting NO_2 concentration, especially for the highest NO_X concentrations which occur close to the emission source.

ARM Version 2 (ARM2) has been developed using 1-h ambient monitoring data to address this variation in the conversion factor as a function of total NO_X concentration. ARM2 is based on observed hourly NO_2/NO_X concentration ratios from a large data set with diverse source-monitor distances, atmospheric ozone concentrations, and atmospheric dispersion conditions. This large measured data set was used to develop an empirical equation that estimates a conservative upper bound of the conversion factor as a function of total NO_X concentration. The performance of the ARM2 method has been evaluated using other, independent monitored data sets as well as comparisons to the EPA Tier 3 conversion methods.

2. Methods

The ambient NO_2 and NO_X monitoring data analyzed to develop ARM2 were extracted from EPA's Air Quality System (AQS) for the period 2001 through 2010 (AQS Online Data, 2013). This 10-year data set contains 1-h average NO_X and NO_2 data from more than 580 ambient air quality monitors located throughout the United States. These monitors are located in both urban and rural areas and have various measurement objectives, including roadway monitoring, source surveillance, and general background monitoring.

The observed NO_2/NO_X conversion factor for each hour at each station was computed. The data were graphed using scatter plots, and the empirical relationships that are observed between the conversion factors and the total NO_X concentration were used to develop the ARM2 equation. This analysis is similar to that described by Scire and Borissova (2011).

The performance of AERMOD and ARM2 was then evaluated using independent data sets. These model evaluation data sets are the Empire Abo (North and South monitoring sites), Palaau, and Wainwright ambient data sets (Evaluation of Bias inR, 2005; Hanna et al., 2012). The data sets consist of hourly averaged NO_2, NO_X, ozone, and meteorological data collected near a gas processing plant, a combustion turbine power generator, and a small diesel-fired IC-engine power plant. Hourly NO_X emissions for some of

the data sets were estimated parametrically, based on available data such as power generation levels. The measured 1-h NO_2 concentrations in these evaluation data sets ranged from background concentrations of a few ppbv up to 67 ppbv for the Empire Abo North site.

The emission and meteorological data were input to AERMOD to calculate hourly total NO_X concentrations at a single receptor representing the location of the ambient monitor. For the PVMRM and OLM methods, the ISRs were assumed to be 0.2. The hourly NO_2 concentrations were then calculated using the ARM2, PVMRM and OLM conversion methods. The model predicted concentrations were input to a spreadsheet, along with the concurrent measured concentrations and wind speed and direction data. The data were sorted by wind direction, and hours were selected when the wind direction was within a 60° sector centered on the direct transport direction from the modeled source to the ambient monitor. This focused the analysis on hours with higher direct impacts from the source at the ambient monitor, and helped reduce the potential confounding effect of other background emission sources on the monitoring data. Only hours where both the modeled and measured NO_X concentration equaled or exceeded 10 ppbv (20 μg/m^3) were analyzed. This threshold avoids the measurement uncertainty that can be significant when NO_X ambient concentrations are low.

Scatter plots were prepared of the model predicted and the observed conversion factors as a function of the NO_X concentration. Quantile–quantile (Q–Q) plots of modeled NO_2 concentrations versus measured NO_2 concentrations were prepared to evaluate the overall ability of the modeling methods to match the frequency distribution of the NO_2 measurements, especially in the higher concentration range near the 1-h NO_2 air quality standard (Perry et al., 2005). The model predicted hourly NO_2 and NO_X concentrations were also compared to measurements using the Robust Highest Concentration (RHC). The RHC represents a smoothed estimate of the highest concentrations (which are of the most importance in a NAAQS compliance modeling analysis), based on a tail exponential fit to the upper end of the concentration distribution (Cox and Tikvart, 1990). The RHC equation is:

$$RHC = x\{n\} + (x - x\{n\})\ln\left(3n - \frac{1}{2}\right)$$

where n is 26 as recommended by Cox and Tikvart (1990), x is the average of the n-1 largest values, and $x\{n\}$ is the nth largest value.

In addition to comparing model predictions to observations, additional modeling was performed to inter-compare the ARM2, PVMRM, and OLM methods across a range of typical meteorology and emission source characteristics (a sensitivity analysis). The scenarios modeled included those previously used in testing of the PVMRM and OLM methods by MACTEC (Sensitivity Analysis of P, 2004), as well as scenarios that are representative of large diesel generators, a refinery, a gas pipeline compressor station, natural gas production fields and processing plants, and a large boiler. The MACTEC single source scenarios analyzed included a diesel generator scenario (stack height of 26 m, exhaust temperature of 727° K, and NO_X emission rate of 40 lbs/h), a natural gas-fired combustion turbine (stack height of 31 m, exhaust temperature of 750° K, and NO_X emission rate of 240 lbs/h), and a generic boiler scenario (stack height of 35 m, exhaust temperature of 432° K, and two NO_X emission rates of 8 and 400 lbs/h). The MACTEC scenarios were modeled assuming an ISR of 0.1 (to match the original MACTEC analysis), in both flat and complex terrain, with rural and urban dispersion coefficients, and with and without aerodynamic stack downwash, to simulate a wide range of source and dispersion characteristics. The “cumulative source scenario” from the MACTEC report was also analyzed, which included a total of 65 point sources and 1598 receptors. The additional scenarios modeled used ISRs of 0.1 for the boiler scenario, and 0.2 for all others.

3. Results and discussion

3.1. Derivation of ARM2 conversion factors

The first step in ARM2 development was to create a scatter plot of the observed hourly conversion factors as a function of NO_X concentration (shown as the blue (in the web version) data points in Fig. 1). A plot of the upper bound of the observed conversion factors as a function of the NO_X concentration has a distinct shape (shown as the red (in the web version) line in Fig. 1), similar to that of a decaying power function. This plot shape is consistent with Chu and Meyer's and Janssen's observations that the conversion factor varies and is limited at higher NO_X concentrations near a source by chemical kinetics and plume mixing rates. Fig. 1 shows that when NO_X concentrations are above about 350 ppbv, the conversion factors are found in a range of 0.1–0.2. It is not known if these higher measured NO_X concentrations represent near-source impacts of NO_X emission sources versus impacts from more distant, larger NO_X sources, and the ISRs of the contributing emission sources are also not known.

Fig. 1 suggests that the upper bound of the NO_X to NO_2 conversion factor as a function of NO_X concentration could be described by an analytical equation. To objectively establish this equation, the data were sorted into NO_X concentration “bins” over the range 20 ppbv–600 ppbv, and the 98th percentile value in each bin was calculated to represent the upper bound of observed conversion factors for each bin. The 98th percentile rather than the maximum value was used because this value is more stable and not subject to extreme variations associated with spurious data points, such as those caused by monitor calibrations and other operations that were not properly flagged and removed in the data base. Using the 98th percentile may remove some valid measurements, but still provides a reasonable estimate of the maximum observed conversion ratio for each NO_X concentration bin. While the selection of the 98th percentile is arbitrary, it will more conservatively estimate the upper limits of conversion for 1-h averages than the 90th percentile value that was used in development of the original annual average ARM method.

The 98th percentile values for each bin were fitted using a polynomial equation. Fig. 1 presents the 98th percentile conversion factor for each NO_X concentration bin (as a red (in the web version) data point), and the resulting ARM2 conversion equation (note that the equation presented in Fig. 1 is based on NO_X concentration units of ppb; because AERMOD outputs NO_X concentrations in units of μg/m^3, the ARM2 equation coefficients coded into AERMOD have been adjusted for the different concentration units). The NO_X to NO_2 conversion factors calculated from this equation were then limited to a maximum value of 0.9 and a minimum value of 0.2. The maximum value is based on EPA's current recommendation for the maximum “equilibrium” ratio of 0.9 for the Tier 3 conversion methods. The minimum conversion factor is based on the data in Fig. 1, as well as consideration that typical NO_2/NO_X ratios for stack emissions from combustion sources are in the range of 0.1–0.2.

In EPA's September 30, 2014 guidance memorandum, EPA notes that the AQS monitoring data used to derive the ARM2 equation is collected at stations that are typically placed to determine the general background levels of air quality in an area, and therefore may not necessarily represent the ambient concentrations and conditions that could occur near a major NO_X emission source. These near-source conditions may include downwash effects and incomplete reaction of NO with ozone because of the short

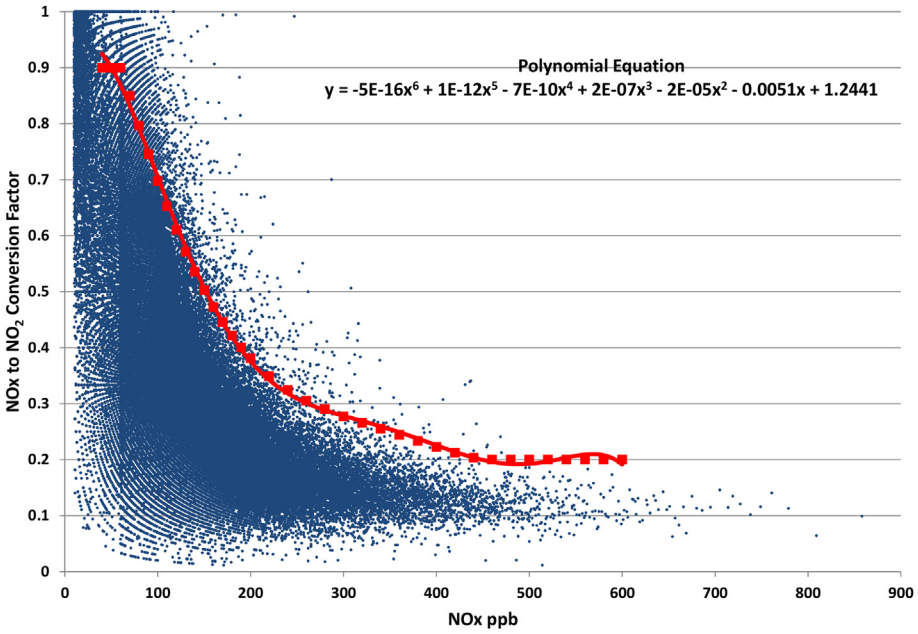

Fig. 1. AQS data NO_2 conversion factors and fitted curve.

transport times to nearby "fence line" locations. Two additional analyses were performed to further investigate this EPA comment.

First, the AQS NO_X monitoring data was reviewed to determine what percentage of the NO_X monitoring stations had a specified objective of "source surveillance", which would indicate that the monitor is located near an emission source. Approximately 5 percent of the monitoring stations reported to the AQS data base in 2010 had a source surveillance objective, therefore approximately 20 of the AQS NO_X monitoring stations are located near stationary sources of NO_X emissions.

Second, some additional ambient NO_X monitoring data was identified from three monitoring stations (AQS Site numbers 560050011, 560090008, and 560130234) that are located at distances ranging from 30 to 500 m from gas processing plants in Wyoming. The objective of these stations are source surveillance, therefore they are representative of ambient NO_X concentrations and conditions that occur immediately next to NO_X emission sources. Approximately 1 year of recent data is available for two of the stations, and 2 recent years at the third station. Fig. 2 plots the observed NO_2 conversion factors at these stations versus the previously derived ARM2 curve. The observed conversion factors are all significantly lower than the ARM2 equation values, except at the lowest NO_X concentration ranges when the ARM2 factor is limited to 0.9. This data indicates that the ARM2 equation conservatively estimates the conversion occurring near these types of NO_X emission sources. The fact the observed factors are lower than the ARM2 predictions may be a result of incomplete plume mixing and/or NO reaction rates with ozone over these short travel distances. This analysis may not characterize near-source impacts from high ISR sources.

3.2. Performance evaluation results

AERMOD version 14134 includes the ARM2 conversion method as a new model option. The performance of ARM2, as well as the Tier 3 PVMRM and OLM methods, was evaluated using three test data sets by comparing the model predicted conversion factors and NO_2 concentrations to measured values. It should be noted that there are some limitations in these test data sets. The modeled NO_X emissions are annualized average rates for the Palaau and Empire Abo data sets rather than hourly estimates, and ISRs were not measured for any of the data sets and a value of 0.2 was assumed. The modeling results are sensitive to these inputs, particularly the ISRs.

Scatter plots of ARM2, PVMRM, and OLM predicted conversion factors, and the observed conversion factors, were plotted as a function of NO_X concentrations. Fig. 3 is for the Palaau data set, and similar relationships are observed in the other test data sets. The PVMRM predicted conversion factors generally are the lowest and closest to the observed conversion factors, while the ARM2 predicted factors generally are the highest estimator of the conversion. However, at the upper end of the NO_X concentration range near the level of the 1-h NO_2 NAAQS, the predicted conversion factors for all three methods cluster in the range of 0.2–0.35, and the observed factors are in the range of 0.1–0.2. This indicates that all three methods similarly overestimate the degree of NO_2 conversion at elevated NO_X concentration ranges.

Fig. 4 is an example Q–Q plot of predicted NO_2 concentrations for the Empire Abo North data set. All the conversion methods under predict NO_2 concentrations at the low end of the distribution. This behavior has been previously noted for the performance of the AERMOD model itself (Perry et al., 2005). In addition, the monitoring data includes background concentrations while the model predicted concentrations do not; this may contribute to the under predictions of the modeled results at low concentrations. Fig. 4 shows that as the observed NO_2 concentration increases, each method begins to predict NO_2 concentrations above the 1:1 line. At the upper end of the observed NO_2 concentrations all methods over-estimate the NO_2 concentrations, with ARM2 and PVMRM resulting in closer agreement to the observations.

The Robust Highest Concentration (RHC) comparison is presented in Table 1. The results are consistent with the relative performance at the upper end of the NO_2 concentration distribution illustrated in the Q–Q plots. The Tier 1 full conversion option (NO_2 assumed to be equal to the AERMOD predicted NO_X concentration) significantly over-predicts the highest NO_2 concentrations by an approximate factor of 5 across all three test data sets. The NO_2 performance of the ARM2, PVMRM, and OLM methods is similar; all

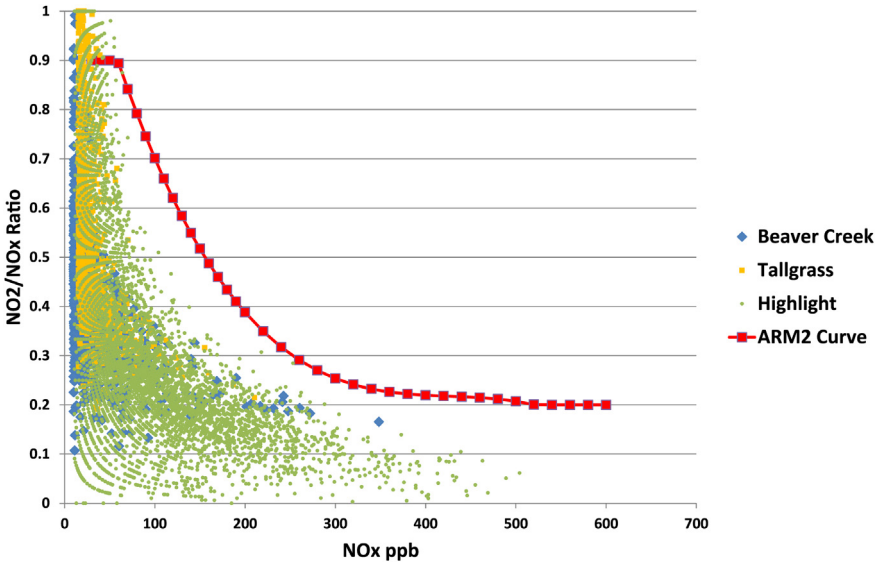

Fig. 2. Near source NO_2 conversion factors and ARM2 curve.

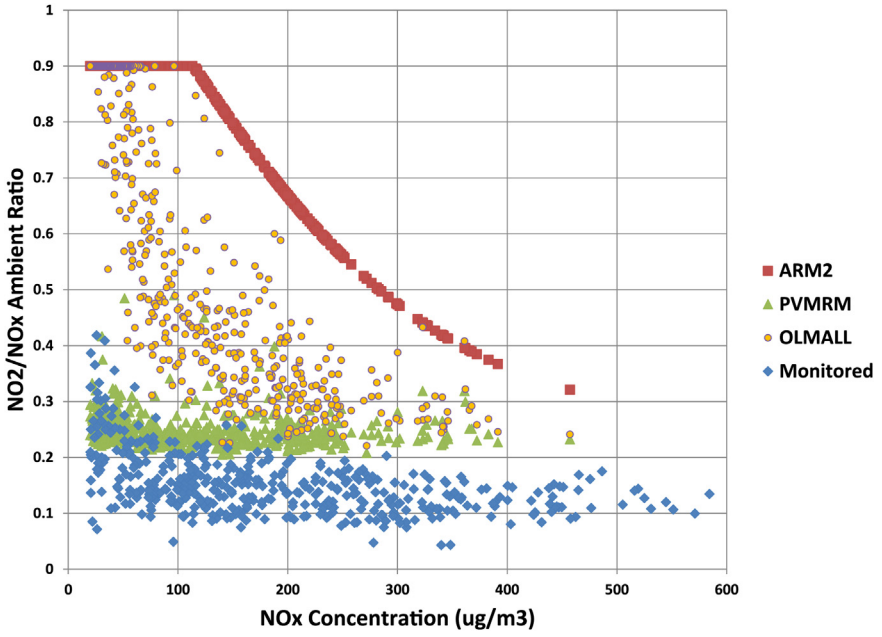

Fig. 3. Conversion Factor vs. NO_X Concentration for Palaau Data Set.

3 methods over-predict NO_2 concentrations by a factor of approximately 1.7–2.0, based on the geometric mean across all the test data sets.

To help separate the effects of AERMOD's accuracy for dispersion estimates from the performance of the NO_2 conversion factor methods, and to help identify potential compensating errors between the dispersion model and the NO_2 conversion methodology, the modeled RHC for NO_X was compared to the observed NO_X RHC. The geometric mean of the AERMOD predicted RHC total NO_X concentration divided by the Observed RHC NO_X concentration across all three data sets is 0.94. This indicates that on average AERMOD underestimates the total NO_X concentration by approximately 6%. However, all of the NO_2 conversion methods overestimate the NO_2 concentration by 70%–100%. This suggests that for these data sets, the NO_2 conversion methodology is the more important element for accurately predicting NO_2 concentrations.

3.3. Method comparison results

Additional model analyses were performed to compare the full conversion, ARM2, PVMRM, and OLM estimated NO_2 concentrations over a wide range of source characteristics and model options. The ISRs used in these analyses were 0.1 for the MACTEC scenarios (to match the original MACTEC analysis), 0.1 for the additional boiler scenarios, and 0.2 for all other scenarios (reasonable estimates for the types of sources modeled). The modeled 1-h NO_2 design concentrations were used for the comparison, which focused the analysis on the model output metric that is required for regulatory decisions. The 1-h NO_2 design concentration has been defined by the EPA as the 98th percentile of the daily maximum 1-

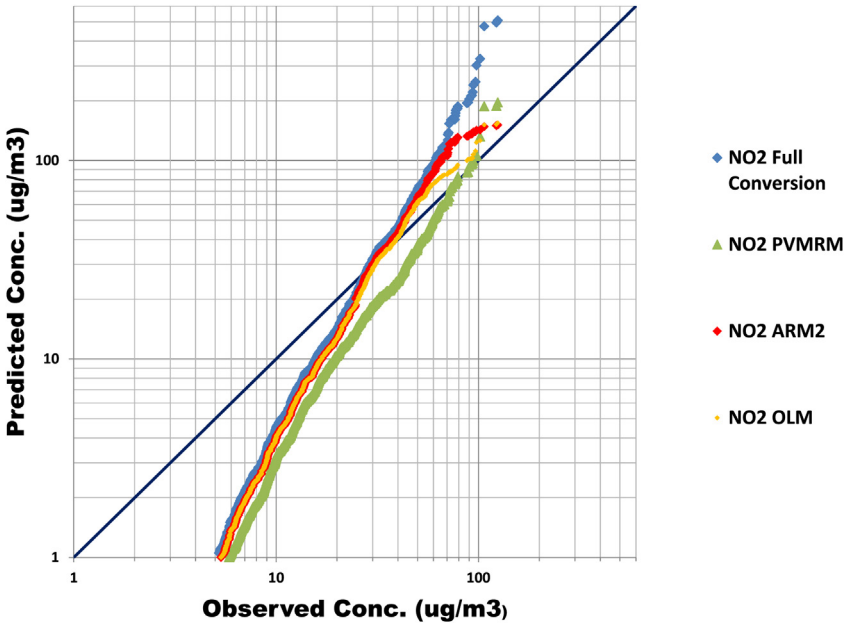

Fig. 4. Q–Q plot for the Empire North NO_2 data set.

Table 1
RHC performance summary.

Test data set	Observed NO_X ($\mu g/m^3$)	Observed NO_2 ($\mu g/m^3$)	NO_2 full conversion ($\mu g/m^3$)	PVMRM NO_2 ($\mu g/m^3$)	OLM NO_2 ($\mu g/m^3$)	ARM2 NO_2 ($\mu g/m^3$)
Empire Abo North	532.5	128.9	436.8	184.2	149.3	165.4
Empire Abo South	462.3	79.9	446.2	264.7	163.9	164.9
Palaau	650.9	93.5	465.1	138.7	166.3	147.7
Wainwright	393.6	82.0	528.1	177.0	169.4	217.7
Geometric mean for predicted versus observed NO_2 RHC	N/A	N/A	4.96	1.97	1.72	1.83

Table 2
Comparison of 1-h NO_2 design concentrations for multi-source scenario.

Conversion method	Maximum NO_2 concentration ($\mu g/m^3$)	Ratio for method concentration versus NO_X concentration
Full Conversion	1774	1
OLM	238	0.13
PVMRM	322	0.18
ARM2	355	0.20

h concentrations, to match the form of the 1-h NO_2 NAAQS.

The ratios of predicted NO_2 to NO_X concentrations for the ARM2,

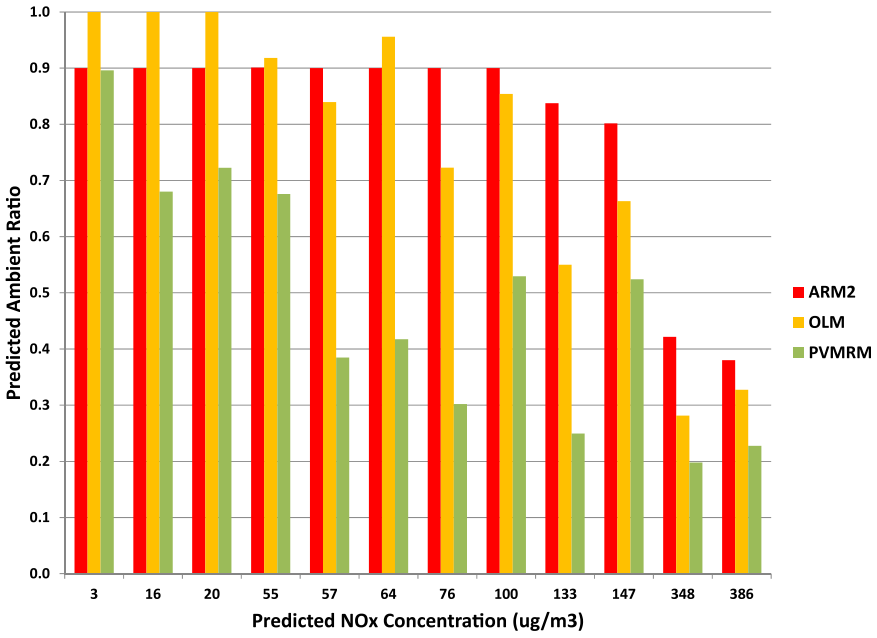

Fig. 5. Single source sensitivity analysis results.

OLM, and PVMRM methods are presented in Fig. 5 for the MACTEC single-source scenarios. For scenarios with modeled NO_X concentrations less than 70 μg/m^3, the ARM2 and OLM ratios were all above 0.8, while the PVMRM ratios ranged from 0.4 to 0.9. For scenarios with modeled NO_X design concentrations of 348 μg/m^3 and higher, the ratios for all methods were in the range of 0.2–0.4. In general, PVMRM predicted the lowest NO_2 concentration for each scenario.

Table 2 presents the results of the sensitivity analysis for the MACTEC multi-source scenario. These results indicate that the modeled NO_2 design concentrations for all three methods are generally similar, with conversion ratios in the 0.1 to 0.2 range.

Table 3 presents the results of the additional multi-source scenarios that were analyzed. These scenarios are based on actual configurations of large diesel-fired power generators, a refinery, a gas pipeline compressor station, natural gas production fields and processing plants, and a coal-fired boiler in complex terrain. Four of the scenarios result in modeled 1-h NO_X concentrations that are moderately high (ranging from 190 to 461 μg/m^3); for these scenarios the ratios of method predicted NO_2 concentration relative to the total NO_X concentration vary from 0.30 to 0.69, with the exception of one PVMRM modeled value of 0.9. The other four modeled scenarios result in modeled 1-h NO_X concentrations that are much higher (ranging from 1080 to 2823 μg/m^3); for these scenarios the ratios vary from 0.15 to 0.34, again with one exception for PVMRM with a ratio of 0.87. These two inconsistent PVMRM cases were further evaluated by additional modeling using a very conservative variation of the OLM method, the “source by source” approach, and this supplemental analysis shows the PVMRM results to be higher than the theoretically more conservative source-by-source OLM method. This suggests that the PVMRM predictions are unrealistic for these two cases. When these two inconsistent PVMRM cases are excluded, the geometric means of the ratios of method predicted NO_2 concentration relative to the NO_X concentration are very similar for all three methods, with values of 0.29 for PVRMR, 0.31 for ARM2, and 0.32 for OLM.

3.4. EPA ARM2 evaluation results

In EPA's September 30, 2014 guidance memorandum, EPA presents some additional evaluations of ARM2. EPA stated that because the field evaluation databases used to test ARM2 were based on emission sources with a relatively low ISR (0.1–0.2) and typical ozone concentrations, the results from the evaluations presented in Section 3.2 did not test ARM2 performance near a source that has a higher ISR and at locations with higher background ozone levels.

EPA conducted theoretical calculations assuming an ISR of 0, total NO reaction with ozone, and pseudo-steady state approximations, using “extreme”, “high”, and “mean” ozone concentration and ambient temperature assumptions. For example, the extreme ozone assumption used an hourly background ozone concentration of 150 ppb (based on 2013 data from all ozone monitoring sites in the US, only one station in California had one hour of data measured at this extreme concentration). EPA noted that because of the combination of assumptions in these theoretical calculations, the computed NO_2/NO_X ambient ratios likely overestimate typical ratios.

When ARM2 was compared to these theoretical calculations, it was shown that under high and mean ozone and ambient temperature conditions, ARM2 conservatively predicted higher ambient NO_2/NO_X ratios than the theoretical calculations. Only under the extreme assumptions did ARM2 predict ratios lower than theoretical calculations. EPA's conclusion was that for areas that regularly experience high hourly ozone levels (persistently above 80–90 ppb) ARM2 should be used with caution.

EPA then performed additional theoretical calculations using a “plume volume” method, described as being similar to the PVMRM method, over a range of ozone concentrations and ISR for the NO_X source emissions. When the ISR was assumed to be 0.5, it was shown that the ARM2 predicted ambient ratios were lower than the plume volume theoretical calculations.

In addition to these theoretical calculations, EPA also compared ARM2 to PVMRM predictions using AERMOD and a range of ISR assumptions for four emission sources. When the modeling included ISRs of 0.5, there were times when the ARM2 predicted ambient ratios were lower than the PVMRM predictions. EPA evaluated increasing the minimum ARM2 ambient ratio by adjusting the default value from 0.2 to 0.5. These results showed that while the ARM2 predicted ambient ratios did increase, there still were hours when ARM2 predicts lower ratios than PVMRM.

In summary, the EPA evaluations used theoretical calculations and a comparison to PVMRM to show that when the ISRs are 0.5, or under extremely high ozone concentrations, there can be times when ARM2 predicts lower NO_2/NO_X ambient ratios than these other methods. While there are no evaluation data sets with actual measurements at these conditions to confirm the theoretical calculations or PVMRM performance, it is reasonable to expect that high ISR emission sources could cause high NO_2/NO_X ambient ratios. Based on these analyses, EPA has developed criteria for the approved use of ARM2 for regulatory 1-h NO_2 NAAQS modeling.

The observed sensitivity of ARM2 and the Tier 3 methods to the assumed ISR highlights the critical need for additional ISR data. The predominate types of sources in the ARM2 test evaluation data sets described in Section 3.2 are compressor engines, and unit-specific ISR data was not available for these units. When a typical value of 0.2 was assumed for these sources, ARM2 agreed well with the actual ambient measurements. EPA has used a conservative ISR assumption of 0.5 for the development of the approval criteria for

Table 3
Comparison of 1-h NO_2 design concentrations for additional scenarios.

Description of scenario	Full conversion μg/m^3	OLM μg/m^3	PVMRM μg/m^3	ARM2 μg/m^3	Ratio for OLM/ Full conversion	Ratio for PVMRM/ Full conversion	Ratio for ARM2/ Full conversion
Refinery Example	190	128	109	132	0.67	0.57	0.69
2600 kW Generators	348	143	103	147	0.41	0.30	0.42
Compressor station	461	205	415	147	0.44	0.90[a]	0.32
Gas Production A	1523	380	524	304	0.25	0.34	0.20
Gas Production B	2823	640	2450	564	0.23	0.87[a]	0.20
Large Boiler @ 1 km	2682	409	463	536	0.15	0.17	0.20
Large Boiler @ 3 km	1080	249	185	216	0.23	0.17	0.20
Large Boiler @ 10 km	402	181	153	147	0.45	0.38	0.37
Geometric Mean[b]	N/A	N/A	N/A	N/A	0.32	0.29	0.31

[a] Inconsistent PVMRM value is likely an artifact of how method was implemented in AERMOD.
[b] The geometric mean is for the six scenarios without the inconsistent PVMRM value.

ARM2. However, none of the boiler or combustion turbine sources listed in EPA's ISR data base (ISR) have an ISR as high as 0.5, and only 4% of the internal combustion engines have an ISR of 0.5 or higher. Therefore, the frequency and types of sources that may have ISRs of 0.5 is currently unknown.

4. Conclusion

The Ambient Ratio Method (ARM), one of EPA's methods for modeling 1-h NO_2 ambient concentrations with AERMOD, has been updated to ARM2 based on the analysis of ambient monitoring data. The ARM2 evaluations indicate that the performance of the method is comparable to EPA's more refined Tier 3 conversion methods PVMRM and OLM, and that all three methods generally overestimate the ambient NO_2 concentrations.

EPA incorporated the ARM2 method as a "beta test" option in AERMOD version 14134. EPA has developed the following criteria for approved use of ARM2 for 1-h NO_2 NAAQS modeling in their September 30, 2014 guidance memorandum:

- The AERMOD modeled total NO_X concentration from the primary source can be used to determine if ARM2 is appropriately conservative, regardless of the ISR of the primary source. EPA recommends a modeled total NO_X concentration threshold of less than 150 ppb (282 $\mu g/m^3$) in areas with background hourly ozone concentrations that exceed 80–90 ppb more than 7 days a year, and a threshold of less than 200 ppb (376 $\mu g/m^3$) in other areas. In such a case, no documentation of the source's ISR would need to be provided for approved use of ARM2.
- If the total modeled NO_X concentration exceeds the thresholds recommended above, then the representative background NO_2 concentration may also be considered to justify a higher threshold for approved use of ARM2. If background NO_2 levels are less than 30 ppb, EPA has provided other recommended thresholds in the September 30, 2014 guidance memorandum. For example, with a background NO_2 concentration of 15 ppb, the total NO_X modeled concentration threshold for approved use of ARM2 is less than 320 ppb (602 $\mu g/m^3$).
- If the total modeled NO_X concentration exceeds all the thresholds recommended above, then the ISR of the primary source must be considered. If an adequate demonstration can be provided that 95% of the short-term NO_X emissions at the primary source have ISRs that are at or below 0.2, then ARM2 is approved for use in 1-h NO_2 NAAQS modeling. This demonstration can be made using actual stack test data for the specific sources, source manufacturer test data, state or local agency guidance, or data available through EPA's ISR database or other public database.

EPA's guidance approves the use of ARM2 for regulatory 1-h NO_2 NAAQS analyses under specified circumstances. It is hoped that ARM2 will help reduce the resources expended by both the regulated community and the reviewing agencies when conducting NO_2 modeling analyses, while still providing conservative estimates of ambient impacts. The evaluations discussed in this paper have identified the sensitivity of ARM2 (and the Tier 3 methods) to the assumed emission source ISR, and highlight the critical need for additional ISR data for NO_2 regulatory modeling.

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References

AQS Online Data. http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm (accessed 15.08.13.).

Brode, R.C.O.A.R., September 30, 2014. Clarification on the Use of AERMOD Dispersion Modeling for Demonstrating Compliance with the NO_2 National Ambient Air Quality Standard. http://www.epa.gov/ttn/scram/guidance/clarification/NO2_Clarification_Memo-20140930.pdf.

Chu, S., Meyer, E., 1991. Use of ambient ratios to estimate impact of NO_X sources on annual NO_2 concentration. In: Annual Meeting of the Air and Waste Management Association, Vancouver, British Columbia.

n 40 Code of Federal Regulations Part 51 Appendix W.

Cox, W., Tikvart, J., 1990. A statistical procedure for determining the best performing air quality simulation model. Atmos. Environ. 24A, 2387–2395.

Evaluation of Bias in AERMOD-PVMRM; Alaska DEC Contract No. 18-9010-12, found at: http://www.epa.gov/ttn/scram/7thconf/aermod/pvmrm_bias_eval.pdf, MACTEC, 2005.

Fox, T., June 28, 2010. Applicability of Appendix W Modeling Guidance for the 1-hour NO_2 NAAQS. http://www.epa.gov/ttn/scram/guidance/clarification/ClarificationMemo_AppendixW_Hourly-NO2-NAAQS_FINAL_06-28-2010.pdf.

Fox, T., March 1, 2011. Additional Clarification Regarding Applicability of Appendix W Modeling Guidance for the 1-hour NO_2 NAAQS. http://www.epa.gov/ttn/scram/guidance/clarification/Additional_Clarifications_AppendixW_Hourly-NO2-NAAQS_FINAL_03-01-2011.pdf.

Hanna, S., Hendrick, E., Tino, V., Egan, B., March 14, 2012. PVMRM and OLM evaluation using a new data set. In: EPA 10th Modeling Conference, Research Triangle Park, NC.

EPA/600/R-08/071 Integrated Science Assessment for Oxides of Nitrogen – Health Criteria, July 2008. EPA.

NO_2/NO_x In-Stack Ratio (ISR) Database. http://www.epa.gov/ttn/scram/no2_isr_database.htm.

Janssen, L.H.J.M., Nieuwstadt, T.F.T.M., Donze, M., 1990. Time scales of physical and chemical processes in chemically reactive plumes. Atmos. Environ. 24A (11), 2861–2874.

Janssen, L.M.J.M., Van Haren, P.F., Van Duuren, H., 1991. Measurements and modeling of reactions of nitrogen oxides in power-plant plumes at night. Atmos. Environ. 25A, 829–840.

Karamchandani, Prakash, Koo, Annie, Seigneur, Christian, 1998. Reduced gas-phase kinetic mechanism for atmospheric plume chemistry. Environ. Sci. Technol. 32 (11), 1709–1720.

Perry, Steven G., Cimorelli, Alan J., Paine, Robert J., Brode, Roger W., Weil, Jeffrey C., Venkatram, Akula, Wilson, Robert B., Lee, Russell F., Peters, Warren D., 2005. AERMOD: a dispersion model for Industrial source applications part II: model performance against 17 field study databases. J. Appl. Meteorol. 44, 694–708.

Rethinking the Ozone Problem in Urban and Regional Air Pollution, 1991. National Academy of Sciences, ISBN 0-309-56037-3.

Scire, J., Borissova, M., 2011. An empirical method for modeling short-term and annual NO_2 concentrations in regulatory models. In: Energy & Environment Conference (EUEC), Phoenix, AZ.

Sensitivity Analysis of PVMRM and OLM in AERMOD, 2004. MACTEC. Alaska DEC Contract No. 18-8018-04, found at. http://www.epa.gov/ttn/scram/7thconf/aermod/pvmrm_sens.pdf.

Wang, Y.J., DenBleyker, A., McDonald-Buller, E., Allen, D., Zhang, K., 2011. Modeling the chemical evolution of nitrogen oxides near roadways. Atmos. Environ. 45, 43–52.